Atty. Docket No. 7969-01
Appln. No. 10/648,572

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Mark C. Cesa et al.	
Serial No.:	10/648,572	Group No.: 1624
Filing Date:	26 August 2003	
Title:	PURIFICATION OF ACETONITRILE BY A DISTILLATIVE RECOVERY/ION EXCHANGE RESIN TREATMENT	Examiner: Ebenezer O. Sackey

DECLARATION UNDER 37 C.F.R § 1.132

Mail Stop RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Dear Sir:

I, Mark C. Cesa, declare that:

1. I am a coinventor of and familiar with the above referenced U.S. Patent Application and am familiar with the final Office Action mailed 11 June 2008 and with the cited references including U.S. Patent 4,362,603 ("Presson et al.") and USP 3,313,726 ("Campbell et al.").

I hereby certify that this correspondence (along with any paper referred to as being attached or enclosed) is being facsimile transmitted or deposited with the United States Postal Service as First Class Mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on

TEORI TRIGGS
SEPT. 17, 2008
Date

Signature

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2. I received a Bachelor of Science degree in Chemistry from Princeton University in 1974. I received a Doctor of Philosophy degree in Chemistry from the University of Wisconsin Madison in 1979. I currently am employed by INEOS USA LLC, a company acquired from BP America in December, 2005. However, I have been employed with INEOS USA LLC and its predecessor companies (including BP Amoco Chemical Company, BP Chemicals Inc., and Standard Oil of Ohio) since 1979 as a chemist, and I am responsible for process chemistry and technical support relating to our acrylonitrile production technology. I am a coinventor of more than 25 patents in the field of organic chemistry with a particular focus on nitrile compounds and related structures.

3. Acetonitrile is produced as a by-product in the production of acrylonitrile. Some "world-scale" acrylonitrile production plants (i.e. ≥ about 200,000 MTA) are equipped with acetonitrile purification sections to recover and purify this by-product. The above identified patent application relates to process for the production of HPLC (high performance liquid chromatography) acetonitrile (i.e. highly purified acetonitrile having a UV cutoff of <190 nm). This process as more fully described in the specification and claims of the application is characterized by two key features, (i) operating the three distillation columns in the acetonitrile purification unit under specific reflux ratios, to obtain a highly pure acetonitrile side stream from the third distillation column, and then (ii) passing the highly pure acetonitrile side stream through an acidic ion exchange resin to further purify said highly pure acetonitrile producing highly purified acetonitrile having a UV cutoff of <190 nm. The claimed reflux ratio parameters are necessary to limit impurities such as acrylonitrile, crotononitrile, and crotonaldehyde. The acidic ion exchange resin is used to limit impurities such as acetamide, oxazole and 2-aminopropionitrile. This combination of treatment steps is necessary in order to obtain the highly purified acetonitrile having a UV cutoff of <190 nm (i.e. HPLC acetonitrile).

4. My employer, INEOS USA LLC operates multiple acrylonitrile plants. In order to illustrate the benefit of the claimed invention over the prior art, samples of acetonitrile were collected from our Green Lake, Texas Plant. These samples of acetonitrile were collected after the acetonitrile product column and prior to the resin bed in the plant. For these samples the distillation columns in the acetonitrile purification section were operated at different reflux ratios. These samples of acetonitrile were analyzed. Similarly collected samples of the acetonitrile were additionally treated using a lab scale Amberlyst 15 resin bed. This was done to obtain "before" and "after" resin bed comparisons for the samples which would illustrate the benefit of the reflux ratio/resin combination in achieving HPLC acetonitrile. The sampling, analyses and resin treatment were all done at my direction and/or under my control.

5. The testing procedure and the results are described in greater detail below.

(A) An acrylonitrile plant was operated using reflux ratios for the Light Ends Column (the 1st Column), the Drying Column (the 2nd Column) and the Product Column (the 3rd Column) both inside and outside the claims of the patent application. Reflux ratios were calculated as set forth in the application on page 7, lines 6 16. As stated above, samples of acetonitrile were collected after the acetonitrile product column and prior to the resin bed in the plant.

(B) Some of the samples, Comparative 2 and Invention Example 4, were treated in an Amberlyst 15 Resin Bed. The resin bed was prepared and the samples tested as follows:

(i) 7.35g of wet Amberlyst A15 Resin (Aldrich, CIS#10719) was placed into chromatography column (diameter of ~1 cm, bed volume of ~9 cm^3).

(ii) The resin was rinsed with 200 mL of deionized water at a rapid flow rate, then with 25 mL of 1 M aqueous sulfuric acid solution at a rate of 2 drops/sec (approx.

0.1 mL/sec); then with 50 mL deionized water at a rate of 2 drops/sec (approx. 0.1 mL/sec), then with 100 mL deionized water at maximum flow rate.

(iii) The resin bed was flushed with HPLC acetonitrile HPLC (Fisher synthesis grade) at a rate of ~4.5ml/min,

(iv) After which the resin bed was filled with 40 ml of the collected samples of acetonitrile and an additional 300 ml of the samples were passed through the resin bed at a rate of ~4.5ml/min and then collected for further analysis.

(C) The samples were analyzed for Acetonitrile Product Quality and UV absorbance as follows:

(i) Acetonitrile Product Quality was measured by UV spectrometry using a 1 cm path length cell.

(ii) UV absorbance was measured as described in the application. See Example 2 beginning at page 15, line 11 of the specification.

6. The reflux ratios and the analytical results for each example are shown in the Table below:

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TABLE

	Comparative Example 1	**Comparative Example 2**	**Comparative Example 3**	**Invention Example 4**
Description of Example	Reflux Ratios outside Claim 1 - no resin bed treatment	Reflux Ratios outside Claim 1 - with resin bed treatment	Reflux Ratios within Claim 1 - no resin bed treatment	Reflux Ratios within Claim 1 - with resin bed treatment
Reflux Ratios				
1st Column Reflux Ratio (Light Ends Column) *[in claim 1, > 3]*	3.09	3.09	#1 6.78 #2 6.84	#1 - 6.78 #2 6.84
2nd Column Reflux Ratio (Drying Column) *[in claim 1, > 3.4]*	2.50	2.50	#1 4.47 #2 -4.31	#1 4.47 #2 -4.31
3rd Column Reflux Ratio (Product Column) *[in claim 1, > 6.4]*	2.85	2.85	#1 7.40 #2 7.25	#1 7.40 #2 7.25
Acetonitrile Product Quality				
Acetamide ppm *[in claim 1, < 0.3 milligrams/liter]*	16.4 (12.8 mg/liter)	0.063 (0.05 mg/liter)	#1 16.9 (13.2 mg/liter) #2 17.3 (13.5 mg/liter)	#1 0.067 (0.052 mg/liter) #2 0.157 (0.122 mg/liter)
Acrylonitrile (ppm)	0.323	0.327	#1 - ND #2 - ND	#1 - ND #2 - ND
Methacrylonitrile (ppm)	ND	ND	#1 - ND #2 - ND	#1 - ND #2 - ND
Crotonaldehyde (ppm)	ND	ND	#1 - ND #2 - ND	#1 - ND #2 - ND
Crotonitrile (ppm)	0.092	0.1	#1 - 0.119 #2 – 0.12	#1 0.111 #2 – 0.129
UV Absorbance (AU) @ shown wavelength				
@ 254 nm	0.0241	0.0167	#1 0.0075 #2 0.0056	#1 0.0000 #2 -0.0010
@ 220 nm	0.1781	0.0943	#1 0.0448 #2 0.0376	#1 0.0114 #2 0.0094
@ 190 nm *[in claim 1, UV cut off < 190 nm ... See note 3]*	2.1045	1.0551	#1 1.7755 #2 1.7588	#1 0.6380 #2 0.6281

Notes:
1. "ND" means "not detected".
2. Measurements "#1" and "#2" taken on the same days 13.5 hours apart.
3. UV cutoff is the wavelength at which the absorbance in a 1 cm path length cell is equal to 1 AU (absorbance unit) using water as the reference cell.

7. A brief description of each example is as follows:

(A) Comparative Example 1 operated at reflux ratios outside of our claimed ranges. The sample of acetonitrile received no resin bed treatment. The acetamide content and the UV cutoff for this sample are outside the ranges of our claim 1.

(B) Comparative Example 2 operated at reflux ratios outside of our claimed ranges. The sample of acetonitrile was further treated in a resin bed. The acetamide content is within the range claimed in claim 1; however, the UV cutoff for this sample is outside the range of our claim 1.

(C) Comparative Example 3 operated at reflux ratios within our claimed ranges. The sample of acetonitrile received no resin bed treatment. The acetamide content and the UV cutoff for this sample are outside the ranges of our claim 1.

(D) Invention Example 4 operated at reflux ratios within of our claimed range. The sample of acetonitrile was further treated in a resin bed. The acetamide content and the UV cutoff for this sample are within the claimed parameters of claim 1 (i.e. acetamide is less than 0.3 milligrams per liter and the UV cutoff is less than 190 nm).

The results shown in the Table illustrate that by operating the plant within the reflux ratio parameters in combination with the ion exchange resin, all as claimed in Claim 1 of the application, acetonitrile was produced with improved purity as evidenced by the data in Table 1 and most significantly by a UV cutoff of less than 190 nm.

8. As disclosed above, I have been a chemist responsible for process chemistry and technical support relating to our acrylonitrile production technology for INEOS USA LLC and its predecessor companies since 1986. In this role, I have been very familiar with the development and evolution of our acetonitrile purification technology including the

process described in U.S. Patent 4,362,603 to Presson et al. (and assigned to the Standard Oil Company, a predecessor company). I am also familiar with USP 3,313,726, which teaches the use of ion exchange resins for treating liquid solutions of chemicals. While Presson et al discloses a distillation scheme for acetonitrile recovery and purification, it does not disclose the reflux loops nor the reflux ratios associated with each distillation column. The distillation columns in the acetonitrile recovery and purification section of an acrylonitrile plant as operated at the time of the Presson et al. did operate with reflux streams. However the reflux ratios of such streams were outside the ranges claimed in our application. As such Comparative Example 1 (reflux ratio outside the scope of claim 1) is representative of the distillation scheme as taught by Presson et al. Further, Comparative Example 2 (reflux ratios outside the scope of claim 1 in combination with the resin bed treatment) simulates the prior art as taught by Presson when coupled with a resin bed as taught by Campbell et al. As shown in the Table and as stated above, neither of these schemes is capable of producing highly purified acetonitrile having a UV cutoff for impurities of <190 nm, as claimed in our patent application.

9. The data in the Table illustrates that there is a benefit in product purity achieved by operating the three distillation columns in the acetonitrile purification section (of an acrylonitrile plant) under the specific reflux ratios claimed in our invention. This is evidenced by a comparison of Comparative Example 1 to Comparative Example 3. The acetonitrile of Comparative Example 3 (reflux ratios within claim 1 with no resin bed treatment) has improved product quality and a lower UV cutoff than the acetonitrile of Comparative Example 1 (reflux ratios outside claim 1 with no resin bed treatment).

10. Lastly, the data in the Table illustrate that there is a benefit to the combination of (i) operating the three distillation columns in the acetonitrile purification section (of an acrylonitrile plant) under specific reflux ratios, to obtain a highly pure acetonitrile side stream from the third distillation column, and then (ii) passing the highly pure acetonitrile side stream through an acidic ion exchange resin to further purify said highly pure acetonitrile. This is evidenced by the improved product quality and a UV cutoff for impurities of <190 nm

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for Invention Example 4 (the claimed combination) when compared to Comparative Examples 2 (reflux ratios outside of claim 1 with resin bed treatment) and Comparative Example 3 (reflux ratios within claim 1 with no resin bed treatment).

11. In the Office Action of June 11, 2008, the Examiner has suggested that the difference between the instantly claimed purity of 99.97% and the 99.8% of Presson et al is not patentably distinct. However, this 0.17% difference (equivalent 1700 ppm by weight), if due to certain materials other than water, could have a significant impact on the UV absorbance of the acetonitrile and could place the acetonitrile outside of HPLC acetonitrile product specifications.

12. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Respectfully submitted,

Mark C. Cesa

Date 16 September 2008